THE DIRECT CHLORINATION OF STARCH

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B. S., Bethany College, 1940

A THESIS

submitted in partial fulfillment of the

requirements for the degree of

MASTER OF SCIENCE

Department of Chemistry

KANSAS STATE COLLEGE
OF AGRICULTURE AND APPLIED SCIENCE

1942

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INTRODUCTION

Since starch is potentially one of the most abundant agricultural products, any chemical process suitable for its conversion into useful chemical intermediates is of practical as well as of theoretical importance.

The use of starch as a raw material is limited by its reactivity. In some reactions and with some reagents starch is stable, while in other reactions the products formed are as stable as starch itself. With still other reagents uncharacterizable products are formed in reactions for which thus far no means have been found for adequate control.

Among organic chemicals one of the most useful classes of compounds consists of organic halides. These derivatives lend themselves readily to numerous reaction types including coupling and replacement reactions. Reactive chlorides of starch would, it is assumed, be valuable in organic synthesis as are other organic halides.

This work is concerned with chlorination of starch by means of elementary chlorine. It will be apparent that the successful direct chlorination of starch would have the advantage of placing starch in the category of chemical raw materials.

REVIEW OF THE LITERATURE

The chlorination of starch would, a priori, involve the displacement of the hydrogen atoms, hydroxyl groups, or both, in the starch molecule with chlorine atoms without changing the principal structure of the starch molecule itself. The literature reveals no records of chlorinated starch having been obtained by either direct or indirect methods of chlorination.

Starch has been treated with chlorine in the past, and various commercial patents have been issued on processes which involve the use of not only chlorine itself but also of compounds which are capable of yielding chlorine. But, insofar as is known, no organic chlorides were obtained in these processes and only oxidation products resulted.

Berquist (1) found that upon heating dry starch in the presence of chlorine gas various dextrins, as well as a thin boiling starch, were obtained. Other reactions of commercial use are ones using sodium hypochlorite (2), hypochlorous acid (4), chlorine dioxide (3), or other such chlorine compounds. These are purely oxidation reactions with no chlorine-containing derivatives being produced. The chlorine dioxide served merely to remove nitrogen and phosphorous containing impurities and did not affect the starch molecule itself.

METHODS

Experimental Procedure

Raw starch was chlorinated directly at both high and low temperatures. At low temperatures a catalyst and wetting agent were used and the reactions were varied as to the amount of wetting agent used, the type of wetting agent, the temperature of the catalyst, the temperature of the reaction, and the time of reaction.

Haworth swelled starch was chlorinated directly at low temperatures with the aid of a catalyst and wetting agent. The reactions were varied with amount of catalyst and wetting agent used and the time of the reaction.

For the high temperature chlorination an oil bath in a tall form beaker was heated with an electric heater. The reaction itself was carried out in a 15 x 150 mm pyrex test tube with a tube sealed into the bottom to carry off the excess chlorine. The reaction system was kept moisture-proof by means of sulfuric acid traps in the lines.

The oil bath was first heated to the desired temperature. About 3 g of soda lime were placed in the bottom of the test tube to absorb any moisture formed by the reaction. Preliminary tests had shown that such moisture interfered with the course of the reaction. About 12 g of dry, raw starch was added either in one mass or dispersed throughout a porous glass wool plug. The tube was then immersed in the heated oil bath and chlorine passed through the reaction at about 40 cc per minute for the desired length of time.

For the low temperature chlorination an apparatus as shown in Plate I was used. Water, heated by the constant temperature heater, was passed through the condenser-like water jacket surrounding the reaction chamber. This chamber could accommodate about 5-8 g of starch for each reaction.

A catalyst was needed at these low temperatures to aid the reaction. Of the possible catalysts examined, tetraethyllead proved to be the most satisfactory. The bubbler for the volatile liquid catalyst was cooled to the required temperature by immersing it in an ice bath in a Dewar flask. If the catalyst was to be heated, it was placed in a box built of celotex insulating board which was heated by a 50-watt bulb in series with a thermostat.

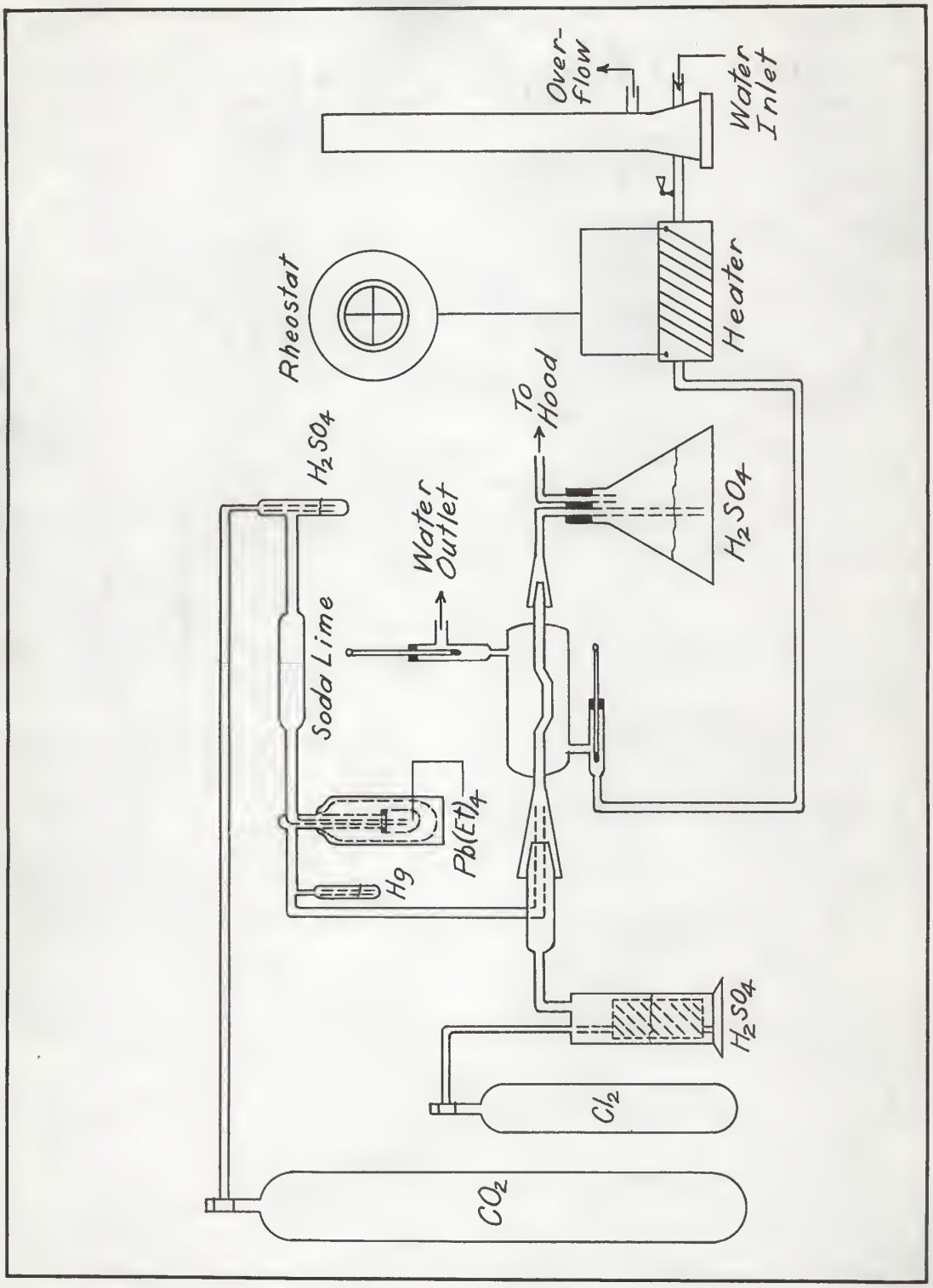
The wetting agents employed here were tetraethyllead and phosphorous oxychloride. If a comparatively small amount of wetting agent were used, the starch was placed in a mortar and the liquid added dropwise with a medicine dropper. The starch was then thoroughly ground with a pestle to assure contact of all the starch with the agent.

Where a large amount of wetting agent was used (i.e. the starch was saturated), as was done with phosphorous oxychloride, the starch was thoroughly mixed with a quantity of the liquid for about half an hour. The excess liquid was then filtered off in an atmosphere of dry air to prevent reaction of the oxychloride with moisture. The wetted starch was then pulverized for the reaction.

EXPLANATION OF PLATE I

Diagram of low temperature chlorination apparatus

PLATE I


Over-
Flow
Water
Inlet
Heater
Rheostat
To
Hood
H_2SO_4
Water
Outlet
H_2SO_4
Soda Lime
$Pb(Et)_4$
Hg
H_2SO_4
Cl_2
CO_2

Since it required only about five minutes to heat the water to the desired temperature, it was found convenient to leave the apparatus disconnected until the wetted starch had been inserted, after which the apparatus was connected to the system.

For the experiments in which tetraethyllead vapor was carried through the reaction chamber, the temperature of the bubbler was brought to the desired point before the system was connected in order to cut down the time between the connecting of the apparatus and the starting of the reaction.

The two types of starches used were raw starch and Haworth swelled starch. Both were dried at 110°C. in vacuuo for 24 hours before using. Unless specific reference is made to the Haworth starch, it will be understood that the raw starch has been used.

The experiments were carried out to determine the optimum conditions of time, temperature, and concentration of the catalyst. The latter was controlled by varying the temperature in the bubbler, thus raising or lowering the vapor pressure of the tetraethyllead. The different reactions were carried out with some property of the system as time of reaction, temperature, or concentration of the catalyst being varied. The concentration of the wetting agent was also changed by adding more or less per gram of starch. Both carbon dioxide and chlorine were added at approximately 25 cc per minute for all reactions.

At the end of the reaction the product was removed and washed with Skelly solve to remove excess tetraethyllead. It was then extracted from five-ten hours with carbon disulfide to remove lead chloride formed by the side reaction of the tetra-

ethyllead with the chlorine and also to remove phosphorous oxychloride, in the event that the latter had been used.

Analysis of the Products

The product, after extraction, was analyzed for chlorine content. A weighed sample was digested in a Parr bomb and the chlorine present was determined by the standard Volhard titration method. In all cases the results of the experiments were recorded in terms of the percent chlorine in the product.

Properties of the Products

The products obtained from the high temperature chlorination differed both physically and chemically from the original starch. The color of the products varied from yellow to dark brown. The light yellow products were insoluble in acetone but soluble with decomposition in s-tetrachloroethane. The dark brown products were partially soluble in acetone. None of the chlorine compounds gave off any odor of chlorine upon heating to the charring temperature of the products.

The chlorinated starch from both high and low temperature chlorination, containing as low as three percent chlorine, upon being coupled with phenol in a Friedel-Craft's reaction and the resulting compound being coupled with a diazotized amine in a basic solution, gave a colored compound. With H-acid this was purple, and with amiline it was brown.

The products of the low temperature chlorination gave the blue color with iodine so characteristic of starch, while the com-

pounds obtained at the high temperatures did not give this color.

RESULTS

High Temperature Chlorination

Dry, raw starch heated to the high temperatures was subjected to the dry chlorine gas with the results shown in Table 1.

Table 1. Variables: Temperature and time.

Temperature: °C.	Condition of starch	Time, hours	Nature of product	Percent chlorine
Above 125	In mass	25	Black, soluble in acetone	14
110	" "	25	Brown	5
110	Suspended in glass wool plug	116	Yellow	32
110	"	216	Yellow	32

Low Temperature Chlorination

When tetraethyllead was bubbled through the system without the starch being first wet with a wetting agent, no matter what the temperature of the catalyst or reaction, the product contained no chlorine.

Two-hour reactions with no tetraethyllead being bubbled through but with the starch wet with four drops of tetraethyllead per gram gave the results shown in Table 2.

Table 2. Variation of temperature of reaction.

Temperature °C.	Nature of product	Percent chlorine
20	White, damp	Trace
30	White, damp	Trace
40	White, dry	4.2
50	White, flaky	3.7
60	Gray	3.4
70	Gray	2.4
80	White	1.5

Tetraethyllead was bubbled through the reactions which ran for five hours each. The starch, wet with 3-4 g of tetraethyllead per gram, gave the results in Table 3.

Table 3. Variation of the temperature of the tetraethyllead.

Temperature of $Pb(Et)_4$ °C.	Percent chlorine
20	1.55
30	1.80
40	2.35

The time was increased to 24 hours with the tetraethyllead being kept at 30°C. The results, with 5 g of starch wet by 40 drops of tetraethyllead, are found in Table 4.

Table 4. Variation of the temperature of reaction.

Temperature of reaction °C.	Percent chlorine
22	5.8
30	4.0
40	4.6

With the reaction at 30°C. and the above conditions the same, the product contained 4.5 percent chlorine after 50 hours of reaction.

These products were all grayish in color. It was found that at room temperature the concentration of tetraethyllead used in these reactions would ignite spontaneously with chlorine causing the product to become somewhat gray.

The amount of wetting agent was cut down to one drop of tetraethyllead per gram of starch. The time was held at 24 hours. The results are given in Table 5.

Table 5. Variation of the temperature of reaction and concentration of tetraethyllead.

Temperature of reaction °C.	Temperature of $Pb(Et)_4$ °C.	Percent chlorine
20	40	1.00
40	50	0.75
50	40	2.85
50	50	0.50
60	40	0.50
60	50	0.50

The wetting agent was changed to phosphorous oxychloride, two drops per gram of starch. Reactions ran for six hours with the tetraethyllead at 30°C. Table 6 shows the results.

Table 6. Variation of the temperature of reaction.

Temperature of reaction °C.	Percent chlorine
40	1.95
50	2.4
60	2.7

Increasing the amount of phosphorous oxychloride used for each gram of starch had no effect on the chlorine content of the product.

Table 7 gives the results obtained when five drops of phosphorous oxychloride were used per gram of starch with the reactions at 40°C. and the tetraethyllead at 30°.

Table 7. Increasing time of reaction.

Time, hours	Percent chlorine
4	1.8
6	1.7
8	1.7
24	3.5

The products from the reactions using the oxychloride as a wetting agent were all gray in color and all emitted a strong garlic-like odor.

Soaking the starch in phosphorous oxychloride and filtering the excess leaves a flaky, gray mass. This, when chlorinated for 24 hours at 30°C. and again at 50° with the tetraethyllead at 30°, gave a compound containing 2.2 percent chlorine for both temperatures.

The Haworth starch wet with three drops of tetraethyllead per gram yielded products comparable with raw starch. The tetraethyllead was kept at 30°. The results are shown in Table 8.

Table 8. Variation of time and temperature of reaction. (Haworth starch)

Time, hours	Temperature of reaction °C.	Percent chlorine
24	30	4.2
24	40	2.8
72	30	3.8
96	30	2.4

Reducing the amount of wetting agent, the Haworth starch wet by 10 drops of tetraethyllead to 8 g with the reaction at 50° gave lower percentages.

Table 9. Variation of time (Haworth starch).

Time, hours	Percent chlorine
24	1.0
12	1.0
6	1.3
3	1.5
1.5	1.5

DISCUSSION

At temperatures around 125°C. or above, starch decomposes when acted upon by chlorine gas. At lower temperatures, in the region of 110°C., dry starch will form a compound with a fairly high percentage of chlorine.

At low temperatures, between 20° and 60°C., a catalyst is required for the rate of chlorination to be appreciable. Tetraethyllead proved to be fairly efficient in this respect. Reactions at temperatures as low as 20°C. gave good results when a high concentration of tetraethyllead was present. As the concentration of tetraethyllead was decreased, the percentage chlorine decreased also, indicating a direct relationship between the initial concentration of the tetraethyllead and the amount of chlorine in the product. Increasing the amount of tetraethyllead introduced by raising its temperature above 40°C. decreased the chlorine content. Lowering the temperature below 40°C. to any extent had the same effect.

The temperature of reaction that gave the best results at high initial concentration of tetraethyllead was between 20° and 30°C. As its concentration was lowered, the best temperature was found to be between 40° and 50°C.

Increase of time up to 24 hours increased the chlorine content, but increase over this time tended to decrease the percentage chlorine present.

Addition of tetraethyllead by bubbling had little if any effect upon the reaction or its products. If any effect was

noted, it was one of a decreased chlorine content rather than an increase.

Phosphorous oxychloride as a wetting agent was of some value; however, it was not as convenient nor as efficient to use as tetraethyllead. The products had a pungent odor indicating the possibility of some addition compound with the oxychloride and chlorinated starch.

Haworth starch gave products of lower chlorine content than raw starch, but their chlorine content was more readily correlated with time and temperature than was the case with raw starch. With high tetraethyllead concentration the percentage chlorine decreased with increase of time. This same comparison was noted with low tetraethyllead concentration, although with correspondingly lower percentages.

The Friedel-Craft's and diazo coupling reactions as well as the fact that the products do not decompose to give off odors of chlorine upon heating indicate that the chlorine is attached directly to the carbon of the starch.

SUMMARY

1. Starch was chlorinated directly at both high and low temperatures. However, much must still be done on control of time of reaction and extent of chlorination. Apparatuses and methods for both types of chlorination were described.

2. A rather highly chlorinated product can be obtained from starch at 110°C. after a long reaction.

3. At low temperatures the chlorination process is so slow that a catalyst and wetting agent are required.

4. Tetraethyllead was found to be the most efficient catalyst and wetting agent.

5. Two types of starch were studied--raw starch and Haworth swelled starch.

6. Both types of starch at low temperatures gave low chlorine content compounds.

7. Proof was shown that the chlorine in even the low chlorine content compounds was attached to the carbon in the starch and was not merely adsorbed.

CONCLUSIONS

The optimum temperature for direct chlorination of starch without catalytic aid was near 110°C., while at lower temperatures the best results were obtained around 40° with the aid of a wetting agent and a catalyst.

The results obtained in these experiments tend to show that the reaction in which tetraethyllead was used as a wetting agent and catalyst was rapid and occurred principally within the first hour, decreasing rapidly thereafter. Increase of time over certain limits tends to decompose the product. The upper limit of the reaction temperature is limited by the temperature of rapid loss of the catalyst, probably through its destruction by chlorine.

ACKNOWLEDGMENTS

Indebtedness is acknowledged to Dr. H. N. Barham for aid in selecting this problem and for advice and suggestions in making the study, and to Mr. M. J. Caldwell and Mr. Edward Stickley for help in constructing special parts of the apparatus.

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